

PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

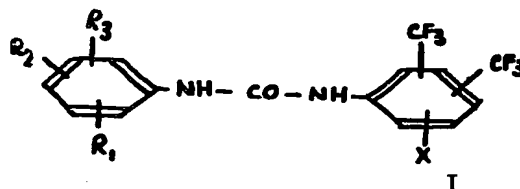
New Diphenyl Urea Derivatives, processes for their production and Compositions containing same

We, J. R. GEIGY A.-G. a body corporate organised according to the laws of Switzerland, of 215, Schwarzwaldallee, Basle, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention concerns a process for the production of new insecticidal and bactericidal derivatives of diphenyl urea which have an affinity to keratin fibres in aqueous dispersion and which protect the treated keratin material from attack and injury by larvae of microlepidoptera (such as moths) and certain species of beetle (such as fur and carpet beetles). The invention also concerns the diphenyl urea derivatives obtained by the production process as well as the pest control agents containing these new compounds as active substances and the use of the new compounds for pest control, in particular for the protection of keratin material from injury by insects and also the keratin material protected in this way from injurious insects. In addition, the invention also concerns disinfectants and disinfectant cleansing agents, in particular textile washing agents and toilet soaps, which contain the new active substances as well as the use of these agents for the disinfection or simultaneous cleansing and disinfection of objects of all types, in particular also of fabrics containing cellulose.

It is known that halogenated diphenyl ureas have antibacterial and insecticidal properties which are particularly marked if there is a CF₃ group in the molecule.

It has now surprisingly been found that substituted diphenyl urea derivatives having two CF₃ groups in one benzene nucleus, of the general formula



wherein R₁ represents hydrogen, a halogen atom, the trifluoromethyl group or the nitro group.

R₂ represents hydrogen, a halogen atom, the trifluoromethyl group or an alkyl or alkoxy radical having from 1 to 5 carbon atoms.

R₃ represents hydrogen, a halogen atom or a phenoxy or phenylmercapto radical possibly substituted by one or more chlorine atoms or alkyl groups having from 1 to 5 carbon atoms, and

X represents hydrogen, a halogen atom or an alkoxy group having from 1 to 5 carbon atoms,

have considerably better insecticidal activity, in particular against insects, in all stages of their development, which are injurious to keratin material such as moth larvae, fur and carpet beetle larvae and, in addition, are suitable, because of their better bactericidal activity, as disinfectant and antibacterial active ingredients for the production of disinfectants and also of disinfectant washing and cleansing agents. In the general formula I, the two CF₃ groups are advantageously in the meta position with regard to each other, in particular in the 3- and 5-positions of the benzene nucleus.

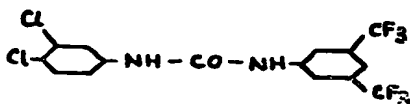
The new diphenyl urea derivatives of the general formula I are produced according to

which contain a higher molecular aliphatic or alicyclic hydrocarbon radical as ring substituent. On stirring such preparations in aqueous treatment liquors, milky dispersions are obtained, from which the diphenyl urea derivatives according to the invention are fixed fast to washing, milling, light and dry cleaning onto keratin fibres, in particular wool, in the warm. Keratin fibres treated in this way with a content of at least 0.1 to 0.5% of active substance are durably protected from injury by larvae of microlepidoptera and certain types of beetle.

Compared with the known, halogenated diphenyl ureas or those containing CF_3 groups, the new compounds having two CF_3 groups in the same benzene ring have the advantage of considerably greater activity, particularly against the injurious larvae of *Attageus* and *Anthrenus* species.

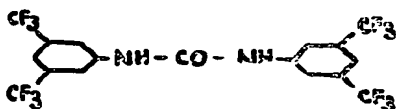
The following examples illustrate the production process according to the invention. Parts are given therein as parts by weight and the temperatures are in degrees Centigrade.

EXAMPLE 1



229 Parts of 3,5 - bis - (trifluoromethyl) - aniline are added to a solution of 188 parts of 3,4 - dichlorophenyl isocyanate (produced by known methods from 3,4 - dichloraniline and phosgene, see, for example, W. Siefken, *Annalen der Chemie*, 562, 96—136, (1948)) in 1000 parts of nitrobenzene. The reaction mixture is heated for 3 hours at 80°. On cooling, the greater part of the diphenyl urea derivative precipitates. It is filtered off under suction and further purified by recrystallisation from methanol. The pure 3,5 - bis - (trifluoromethyl) - 3',4' - dichloro - N,N' - diphenyl urea melts at 210—212°.

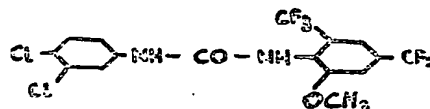
EXAMPLE 2



229 Parts of 3,5 - bis - (trifluoromethyl) - aniline are dissolved in 800 parts of acetone. Phosgene is introduced into this solution at 35—40° and at the same time a solution of 190 parts of sodium acetate in 500 parts of

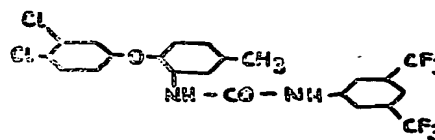
water is added dropwise. Phosgene is introduced until the solution just becomes weakly acid. The reaction mixture is then diluted with water and the precipitate which forms is filtered off under suction. After washing with water it is recrystallised from methanol. The melting point of the pure 3,5,3',5' - tetra - (trifluoromethyl) - N,N' - diphenyl urea is 242—243°.

EXAMPLE 3



259 Parts of 2 - methoxy - 4,6 - bis - (trifluoromethyl) - aniline are dissolved in 600 parts of chlorobenzene and 188 parts of 3,4 - dichlorophenyl isocyanate are added to this solution dropwise at 60°. The reaction mixture is kept for 4 hours at 60—65° and then cooled whereupon the greater part of the reaction product precipitates in crystalline form. It is filtered off under suction and, in the crude form, melts at 200—210°. The pure compound is obtained by recrystallising twice, first from chlorobenzene and then from isopropanol. It then melts at 220—222°.

EXAMPLE 4

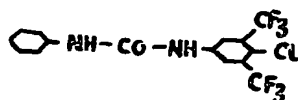


A solution of 252 parts of 3,5 - bis - (trifluoromethyl) - phenyl isocyanate in 2000 parts of chlorobenzene is added dropwise to a previously prepared solution of 278 parts of 2 - amino - 4 - methyl - 3',4' - dichlorodiphenyl ether in 1000 parts of benzene. The mixture is heated for 6 hours at 80—85°. After cooling, the crude product is filtered off under suction and, after drying in vacuo, it melts at about 180°. The compound is purified by recrystallising twice from chlorobenzene and then melts at 190—192°.

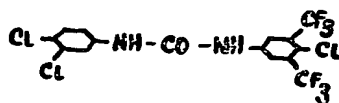
The following compounds can be produced as described in the previous examples from carbonic acid derivatives, and corresponding starting materials of formula II or their isocyanates, and 3,5 - bis - (trifluoromethyl) - aniline; wool treated with these compounds is protected from injury by the larvae of moths, fur and carpet beetles.

	diphenyl urea derivative	M.P.
		202-203°
		208-210°
		190-192°
5		184-186°
		171-172°
		176-177°
		181-183°
		196-198°
10		188-190°

M.P.



185-191°



223-225°

5 The diphenyl urea derivatives of formula I
 10 produced by the process described have considerable affinity to keratin material and are
 15 excellently suitable, therefore, for the protection of keratin material from injury by insects,
 particularly for the fast-to-washing mothproofing of such types of materials, both in the
 raw and processed state, e.g. of raw or processed wool as well as other animal hairs, fells
 and furs. In addition, these compounds can be employed for the impregnation of wool and
 woollen articles whereby excellent mothproofing is also attained.

20 Apart from their insecticidal activity against the larvae of the clothes moth, the compounds
 of formula I also have such action against the larvae of the fur and carpet beetles that keratin
 materials such as blankets, woollen carpets, woollen underwear, woollen clothes and knitted
 goods treated with the compounds according to the invention are protected against all types
 25 of injurious insects.

An example is given below of the application of the new active ingredients.

EXAMPLE 5

30 0.2 Parts of the compound according to example 1 are dissolved in 5 parts of glycol
 monomethyl ether. 5 Parts of sulphonated castor oil are added to this solution which is
 then diluted to 6000 parts by volume with water. 200 Parts of wool are introduced into
 35 the cold dispersion obtained and it is then slowly brought to the boil, and finally boiled
 for one hour. After rinsing and drying in the usual way, the wool so treated proves to be
 completely resistant to attack by the larvae of moths and *Attagenus* and *Anthrenus* species.

40 Apart from the insecticidal activity, the compounds of formula I according to the invention
 have also a very good bactericidal action.

45 For most purposes for which antibacterial active substances are used for disinfection,
 whether for the purpose of simultaneous cleansing or only for disinfection itself, it is important
 that the active substances retain their activity in the presence of capillary active
 50 substances. This is the case with the compounds used according to the invention as
 active substances so that they are excellently

suitable for incorporation into disinfectant washing and cleansing agents as well as into
 disinfectants which in their composition also contain capillary active substances which do
 not serve the purpose of cleansing, for example emulsifying and dispersing agents.

For the production of disinfectant washing and cleansing agents, the active substances of
 general formula I used according to the invention are incorporated in a finely distributed
 form or possibly dissolved in organic solvents into the cleansing agents which have possibly
 been kept in a liquid condition. In particular, capillary active substances of an anion active
 type such as alkali metal soaps or ammonium soaps of fatty acids having from 10 to 20
 carbon atoms, salts of alkyl sulphuric acids or of aliphatic or aromatic sulphonic acids;
 cation active substances such as quaternary ammonium compounds having at least one
 aliphatic or araliphatic radical, the aliphatic portions of which contain from 10 to 20
 carbon atoms, as well as non-ionogenic substances such as the condensation products of
 ethylene oxide with alkanols having from 10 to 20 carbon atoms, with alkyl phenols or with
 partial fatty acid esters of polyhydroxy compounds such as, e.g. sorbitan, are used as
 washing and cleansing agents.

Agents which are only intended for disinfectant purposes can be solutions, suspen-
 sions or emulsions which, apart from the active substances used according to the inven-
 tion, possibly also contain capillary active substances, for example of the type given
 above. Preparations of semi-solid, ointment-like consistency can also be used as disinfect-
 ants. Disinfectants according to the invention can be applied by painting or spraying the
 objects to be disinfected with the preparation concerned. It is also sometimes possible to
 dip the objects into the preparation.

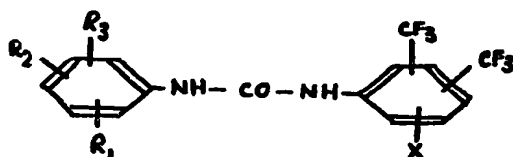
Contents of a few percent of active substances used according to the invention in the
 disinfectant, washing or cleansing agents, and of fractions of percentages in the disinfectant
 application liquors possibly used for simultaneous cleansing, are sufficient to attain effective
 disinfection.

EXAMPLE 11

An antibacterial skin cream is obtained by thoroughly mixing the following components:
 13 parts of glycol monostearate, 1 part of
 5 sodium dodecyl sulphate, 2 parts of polyethylene glycol 1500, 3 parts of wax, 3 parts of viscous paraffin oil, 2 parts of wool fat, 3 parts of polyoxyethylene sorbitan mono-oleate, 6 parts of glycerine, 0.1 parts of perfume, 0.1
 10 parts of p-hydroxybenzoic acid methylester, 2 parts of 3,5 bis - (trifluoromethyl) - 3',4'-dichloro - N,N'-diphenyl urea. Instead of 3,5 - bis - (trifluoromethyl) - 3',4'-dichloro - N,N'-diphenyl urea, also 3,5 - bis - (trifluoromethyl) - 4'-chlorodiphenyl urea can be used.

WHAT WE CLAIM IS:—

1. Process for the production of insecticidally and bactericidally active derivatives of diphenyl urea of the general formula



I

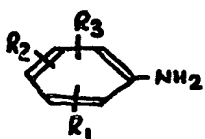
wherein R₁ represents hydrogen, a halogen atom, the trifluoromethyl group or the nitro group,

25 R₂ represents hydrogen, a halogen atom, the trifluoromethyl group or an alkyl or alkoxy radical having from 1 to 5 carbon atoms,

30 R₃ represents hydrogen, a halogen atom or a phenoxy or phenylmercapto radical possibly substituted by one or more chlorine atoms or alkyl groups having from 1 to 5 carbon atoms,

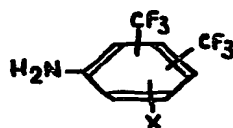
35 X represents hydrogen, a halogen atom or an alkoxy group having from 1 to 5 carbon atoms,

40 which comprises reacting by known methods, possibly in steps and in any order desired, one mol of a reactive derivative of carbonic acid with one mol of each of two aminobenzene compounds of the general formulae



II

and



III

45 wherein R₁, R₂, R₃ and X have the meanings given above.

2. Process according to claim 1 for the production of 3,5 - bis - (trifluoromethyl) - di-

phenyl urea derivatives, which comprises using a 3,5 - bis - (trifluoromethyl) - aniline possibly substituted by a halogen atom, as starting material of the general formula III. 50

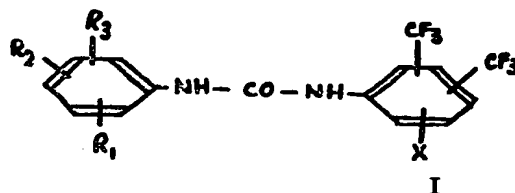
3. Process according to claim 1 for the production of symmetrically substituted diphenyl urea derivatives which comprises reacting 1 mol of a reactive derivative of carbonic acid, in particular phosgene, with 2 mols of a compound of the general formula III given in claim 1. 55

4. Process for the protection of keratin material from injurious insects, which comprises treating the material with agents which contain diphenyl urea derivatives of the general formula I given in claim 1. 60

5. Agents for the protection of keratin material from injurious insects, characterised by a content of diphenyl urea derivatives of the general formula I given in claim 1, such derivatives being in a finely distributed form, possibly combined with suitable carriers or solvents and/or distributing agents. 65

6. The keratin material protected from injurious insects by the use of compounds of the general formula I. 70

7. Diphenyl urea derivatives of the general formula 75



I

wherein R₁, R₂, R₃ and X have the meanings given in claim 1.

8. The manufacture of a disinfectant and disinfectant cleansing agent wherein at least one bacterial diphenyl urea derivative of the general formula I given in claim 1 is mixed with a capillary active agent. 80

9. A disinfectant and disinfectant cleansing agent comprising as active ingredients at least one bactericidal diphenyl urea derivative of the general formula I given in claim 1 and a capillary active agent, especially a cleansing agent. 85

10. A disinfectant and disinfectant cleansing agent according to claim 9 wherein the active ingredient is 3,5 - bis - (trifluoromethyl) - 3',4'-dichloro - N,N'-diphenyl urea. 90

11. A disinfectant and disinfectant cleansing agent according to claim 9 wherein the active ingredient is 3,5 - bis - (trifluoromethyl) - 4'-chloro - N,N'-diphenyl urea. 95

12. A disinfectant and disinfectant cleansing agent according to claim 9 wherein the capillary active agent is an alkali metal soap of fatty acids having from 10 to 20 carbon atoms. 100